Oxidative Pretreatment of Illinois No. 6 Coal: Material and Energy Balances

F. N. Gromicko, L. Saroff, S. Gasior and J. Strakey

U. S. Department of Energy Pittsburgh Energy Research Center 4800 Forbes Avenue Pittsburgh, PA 15213

INTRODUCTION

One of the difficulties encountered when gasifying caking coals is the tendency of the coal to agglomerate. The SYNTHANE process, developed at the Pittsburgh Energy Research Center, incorporates a mild oxidation pretreatment step which destroys the agglomerating characteristic of the coal before entry into the gasifier. The fluidized-bed or entrained pretreater is connected directly to the gasifier and operates at the same pressure. The pretreater products (hot pretreated coal (char) gases, and tar vapors) are fed directly into the gasifier. Consumption of carbon in this step is not detrimental to the process economics. If the oxidative pretreatment were eliminated, additional oxygen would have to be added to the gasifier to heat the coal to the pretreatment temperature. Oxidative pretreatment is presently being studied in entrained-flow and fluidized-bed PDU reactors. Batch fluidized-bed tests have been studied by Forney, et al. (1) and continuous fluidized-bed experiments were described by Gasior, et al. (2). Coal pretreatment tests in an entrained state have been carried out and reported by Saroff, et al. (3).

Experiments have been designed to determine the operating characteristics of entrained-flow and fluidized-bed reactors. Actual experimental data from each reactor are organized and reported as material and energy balances. Operating parameters and process stream compositions are discussed for three sets of data: 40-atmosphere entrained-flow, 40-atmosphere fluidized-bed and 70-atmosphere fluidized-bed. Entrained-flow data has been based on a typical run from a series of 10 similar experiments. Fluidized-bed data are a composite of four similar experiments at each operating pressure. Typical material balances are generated from this data. These balances can be used as a design basis for the pretreatment steps in a gasification plant. Similar balances have been prepared to describe the pretreatment step in the IGT hydrogasification process (4).

EQUIPMENT DESCRIPTION

Entrained Reactor

The entrained pretreatment system, Figure 1, consists primarily of a coal hopper, a process gas heater, a transport line reactor, and a pretreated coal receiver. The reactor is equipped with full instrumentation to permit the measurement of gas flows, operating pressures, pressure differentials, and temperatures at various points in the process. Sample points are provided for the product gas and char. Coal is fed from the hopper by a rotating perforated disc feeder. As each perforation passes the discharge line a synchronized injection of gas forces the coal into a take-off pipe. Coal flow rates are determined by hopper weight losses which are monitored on a tension load cell.

The entrained reactor is a 1/4-inch, 304 stainless steel pipe shaped as an inverted U, 76 feet in length, with auxiliary heaters along its entire length. The heaters are used to minimize heat losses. Temperature measurements are made with chromelalumel sheathed thermocouples. System pressure is monitored on calibrated bourdon tube gauges.

The product gas exits through a particle disengagement zone. Residual dust particles are filtered from the gas which is then passed through a heat exchanger to remove moisture and any other condensables. The pretreated coal is collected in a vessel equipped with a screw extractor to permit sampling under pressure. A product gas sample point and an exit gas meter complete the unit.

Fluidized-bed Reactor

The fluidized-bed pretreater is shown in Figure 2. In many respects this system is similar to the entrained unit. The coal feed mechanism is identical. Process nitrogen is heated prior to carrying the coal into the pretreater vessel. The pretreatment vessel is a 1" schedule 80, 304 stainless steel pipe approximately 10 feet in length. Electric heaters are provided to insure adiabatic operation. Temperature is monitored by four thermocouples. Pretreated coal exits from the top of the pretreatment vessel and falls into the receiver. Fine dust particles are removed by a filter. Water and tars are condensed from the gas stream which is then sampled. The unit is equipped with instrumentation to permit accurate observation and control of all inlet and outlet process streams.

EXPERIMENTAL PROCEDURE

Entrained Reactor

Experiments were conducted solely with Illinois #6 coal ground to minus 20 mesh, with approximately 30% through 200 mesh. Complete proximate-ultimate, ash, and particle size analyses were carried out for each feed. A typical analysis is shown in Table 1. Coal was weighed and charged to the coal hopper prior to the run, and any residual coal in the hopper at the end of the run was weighed to accurately determine the average coal feed rate.

All of the entrained pretreater tests were run at 40 atmospheres pressure. The coal hopper was pressurized independently of the remaining part of the unit. After sealing the entire unit, the back pressure regulator was set at the desired operating pressure and the unit was pressurized.

The transport gas, nitrogen, was heated to 450° C and adjusted to the proper flow rate. The transport line heaters were set to minimize heat losses along the entire reaction length. The speed of the rotating feeder disc was adjusted to give the desired coal feed rate. Shortly after establishing a consistent coal rate, oxygen, at a predetermined flow rate, was introduced to the system. When stable conditions, as evidenced by constant temperatures, were reached, periodic gas and pretreated coal samples were taken. The gas samples were analyzed for 0_2 , CO, CO, CO, CH, and higher molecular weight hydrocarbons. Representative pretreated coal (p.c.) samples were taken at the end of the run and completely analyzed.

Fluidized-bed Reactor

The fluidized-bed unit was operated at both 40 and 70 atmospheres total pressure. The back-pressure regulator was set and pressurization proceeded similar to the entrained process. Nitrogen was heated between 360 and 380°C and adjusted to the desired flow rate. Oxygen was then added down stream of the heater to form the gas mixture that transports the coal to the reaction vessel. Adiabatic settings were maintained on the vessel heaters. Coal feed was initiated and a fluidized-bed was developed in the 10-foot-long vessel.

The exit gas was continuously monitored for oxygen content. Spot samples were analyzed for carbon oxides, CH, and higher molecular weight hydrocarbons. Pretreated

coal dropped from the top of the fluidized-bed and was collected in the receiver. Representative samples of this coal were analyzed at the conclusion of the run. Water and tar were collected, sampled, and analyzed.

In all tests, nitrogen was used as the transport medium. For a commercial-scale plant, steam would be used to transport the coal, since it can be easily removed by condensation, and therefore does not dilute the product. Furthermore, in a commercial facility, lower fluidization velocities would be employed.

DISCUSSION OF RESULTS

Material Balances

Actual mass balances for each unit are presented in Figures 3, 4 and 5. In order to facilitate comparisons between the tests, elemental balances were based on 100 pounds of raw coal. Tables 2, 3 and 4 show the input and output as elemental balances. These elemental balances were scaled upward to a 100 lb. basis from the operating parameters given in Figures 3, 4 and 5. The feed coal was subdivided into three components: free moisture, water of hydration and the remaining coal. Free moisture was determined using ASTM analysis procedures. The water of hydration, held by the clay materials in the coal, was estimated to be 8 weight percent of the ash taken on a moisture-free basis, as discussed by Given (5). Hydrogen and oxygen shown in Tables 2, 3 and 4 were appropriately adjusted to account for the changes in the ultimate analysis caused by the water of hydration assumption. Due to the high operating temperatures of these processes, all of the water of hydration was broken free from the clay materials in the char. Therefore, water of hydration does not appear in the output section of the elemental balances. Corrections for the water of hydration will be important in calculating exit temperature from the enthalpy balance. If the water of hydration was ignored, additional water would appear to be formed during the reaction step, thus a higher exit temperature would be predicted.

Exit stream compositions were examined for each test. The entrained reactor had virtually no tar present at the process exit. Typical tar analyses were used for the 40-and 70-atmosphere fluidized-bed tests. Tar production generally ranged from 1 to 3% of the feed coal, with an average of 1.4% for the 40-atmosphere tests. In the 70-atmosphere tests, tar production ranged from 1 to 5% with an average of 3.2%.

Table 5 shows actual exit gas concentrations for the three processes. Oxygen breakthrough occurs in the entrained pretreater, probably due to the short coal residence time which requires a higher initial partial pressure of oxygen in the feed. The fluidized-bed reaction produces a larger variety of gaseous products such as methane and other hydrocarbons. These gas analyses were incorporated into the material balances.

Closure on the overall mass balances, calculated on a nitrogen gas-free basis, ranged from 93.6% in the 40-atmosphere fluidized-bed run to 99.9% in the 70-atmosphere fluidized-bed experiment. Carbon and hydrogen closures are generally good, with the oxygen being furthest from closure. Poor oxygen closures were probably caused by the analysis technique for the coal and char. Oxygen content is determined by difference, thereby incorporating all of the analysis errors into the oxygen term. Volborth, et.al., (6) describe a method for direct determination of oxygen which may lead to better oxygen closure. These actual balances were composites of data from several similar tests.

When presenting a process flow sheet of any reactor system, it is necessary to have input and output mass flow rates that are totally balanced. This has been achieved by making minor adjustments in the typical balances presented to form design-basis material balances. The char is one of the most difficult streams to measure accurately. There are a number of locations in the process, such as the disengagement zone, where char can become trapped and therefore omitted from the complete balance. In addition, truly representative samples of the char may not always be obtained. Thus elemental balances were brought to complete closure by adjusting the ultimate analyses of the char stream. This led to new ultimate analyses which were within the range of results generally seen for the process.

The completed design-basis mass balances are shown in Figures 6, 7 and 8, and the design-basis elemental balances are given in Tables 6, 7 and 8. These balances have been developed using a large number of pretreatment runs and can be viewed as a good approximation of the material that would be fed to a gasifier after the coal pretreatment step has been accomplished.

Energy Balances

Energy balances were completed for both fluidized-bed tests and the entrained reactor test using the material balances based on actual operating data. The calculations were completed by employing Hess' Law. All the reactant enthalpies were calculated at base temperature, 25° C. Process gas inlet temperatures were generally around 450° C for the entrained reactor and between 360° C and 380° C for the fluidized-bed reactor. The raw coal was always fed at 25° C, so no initial enthalpy term for this coal enters into the balance.

A simple group of reactions was used to describe the overall reaction step at 25° C. Table 8 shows the reactions that were considered. The largest enthalpy changes resulted from the formation of carbon dioxide and water. Contributions from the other components were small, mainly due to the low concentrations. The total enthalpy available can be used to predict the process exit temperature.

Determination of exit temperature involves heating all of the process gases present in the outlet stream and heating of the char. The latent heat of vaporization of water from 25° C to the exit temperature was also included. Table 10 shows a comparison of calculated outlet temperatures and the measured exit temperatures. The fluidized-bed tests were carried out at almost totally adiabatic conditions as was planned. Comparing the calculated temperature with the exit temperature for the entrained pretreater indicates that an adiabatic system was not attained. Due to certain material limitations in the experimental equipment, the char receiver cannot be operated at reaction temperatures. Therefore the insulation on the last 25 feet of the transport line was removed to prevent excessive temperatures in the char receiver. In doing this, an appreciable amount of heat is lost, accounting for the non-adiabatic operating conditions and lowered exit temperature.

Supplemental Analyses

Several other parameters were briefly examined to more completely characterize the two pretreatment processes. A measure of the success of the pretreatment process is its ability to destroy the agglomeration tendency of caking coals. The free swelling index, FSI, is often the parameter used to distinguish a raw caking coal from a treated non-agglomerating char. Table 11 gives FSI's for the raw and treated coals that were studied. The 70 atmosphere reactor was the most successful producer of a non-caking, FSI=0, coal. The remaining two tests did not pretreat the coal completely. Fluidized-bed tests at 40 atmospheres pressure have reduced

the FSI of raw coal to less than the value given in Table 11. A higher operating temperature of approximately 420° C is required for this reduction. The test presented here was operated at only 400° C, thus accounting for the higher free-swelling index. However, the material balance for a 420° C fluid-bed pretreater does not change appreciably from a 400° C reactor.

The carbon consumption during the pretreatment reaction is also noteworthy of examination. In this study, the percentage carbon consumption is determined as the ratio of carbon in the exit tar and gas streams to the carbon in the feed coal. For all of the 40-atmosphere tests, regardless of reactor type, the carbon consumption ranged from 1.9 to 3%. However, in the 70 atmosphere fluidized-bed reactor, a carbon consumption of 10.4% was observed. Tar production in the 70-atm. test consumed 6.2% of the feed carbon, while the product gases accounted for the remaining 4.2% of the conversion. Differences in carbon consumption are probably due to the variation in coal residence times.

Table 12 provides the proximate analyses of the coal before and after the pretreatment reaction takes place. In each instance, the volatile matter is decreased in the process. This can lead to some of the tar formation, and is probably a factor in reducing the agglomeration tendency.

The sulfur forms in the coal before and after pretreatment in the entrained reactor are shown in Table 13. The process does not affect the overall sulfur in the coal to any great extent.

CONCLUSION AND SUMMARY

The oxidative pretreatment of Illinois #6 coal has been studied in two types of reactors: a short residence time entrained-flow unit and a longer residence time fluidized-bed unit. The entrained reactor was operated at 40 atmospheres pressure and the fluidized-bed reactor was tested at both 40 and 70 atmospheres pressure. Material balances were constructed using the raw data gathered in both processes. The 70- atmosphere fluidized-bed and the entrained reactor experiments had closures of 95% or better, while a closure of 94% was calculated in the 40-atmosphere fluidized-bed test. Individual elemental balances varied, carbon and hydrogen recovery were excellent and oxygen recovery generally was the poorest. Typical material balances that can be used for design calculations were generated from the data. Energy balances based on these material balances indicated that the fluidized-bed reactor was operated at almost total adiabatic conditions. Some heat loss was seen in the entrained reactor and linked to the cooling of the process stream at the end of the reactor to protect the char receiver.

Both pretreatment schemes were successful in destroying a large portion of the coal's agglomerating tendencies, as indicated by the free swelling index of the treated coal samples. Tar formation in the entrained reactor was found to be negligible. In the fluidized-bed reactor, 1 to 5% of the feed coal was converted to tar compounds. The work completed and described should prove useful in providing an accurate description of input feed compositions to the gasifier which would be encountered in gasifying caking coals.

Table 1. - Typical Illinois #6 Coal Analysis

Proximate-Ultimate

	Coal(as_received),	wt.
Moisture	6.2	
Volatile Matter	39.3	
Fixed Carbon	43.5	
Ash	11.0	
н	5.3	
С	64.3	
N	1.2	
S	3.4	
0	14.8	
Ash	11.0	

Particle Size

Ash Analysis, %

Silica	47.03	Sieve Size	wt. % Retained on Sieve
A12 ⁰ 3	18.07	20	0
Fe ₂ 0 ₃	18.46	50	9.2
TiO,	1.04	100	30.9
CaO CaO	7.29	140	14.9
MgO	1.03	200	18.3
Na 20	0.86	325	25.0
к ₂ о	1.83	PAN	1.7
so_3^{-2}	4.38		

Table 2. - Actual Entrained Reactor Elemental Balance, wt.

Input							
	Н	С	N	s	0	Ash	Total
Coal Moisture in coal Water of hydration Oxygen feed	4.26 0.78 0.11	62.78	1.12	3.63	7.65 6.22 0.89 11.18	12.56	92.0 7.0 1.0 11.18
Total	5.15	62.78	1.12	3.63	25.94	12.56	111.18
Output							
Pretreater coal, pc Moisture in pc Condensate Product gas	3.64 0.41 0.87	1.19	1.0	3.74	8.66 3.29 6.96 2.93	13.57	91.15 3.7 7.83 4.12
Total	4.92	61.73	1.0	3.74	21.84	13.57	106.8
Recovery, %	95.5	98.3	89.3	103.0	84.2	108.0	96.1

Table 3. - Actual 40-Atmosphere Fluidized-Bed Elemental Balance, wt.

Input	Н	С	N	S	o	Ash	Total	
Coal Moisture in coal Water of hydration Oxygen feed	4.5 0.69 0.1	64.25	1.22	3.47	8.4 5.51 0.79 8.64	11.07	92.91 6.2 0.89 8.64	
Total	5.29	64.25	1.22	3.47	23.34	11.07	108.64	
Output								
Pretreated coal, po Moisture in po Condensate Product gas Tar	3.73 0.07 1.12 0.09 0.11	1.96 1.04	1.0	2.99 0.24 0.06	7.47 0.6 8.92 4.43 0.09		82.97 0.67 10.04 6.72 1.30	
Total	5.12	59.41	1.0	3.29	21.51	11.37	101.7	
Recovery, %	96.8	92.5	82.0	94.8	92.2	102.7	93.6	

Table 4. - Actual 70-Atmosphere Fluidized-Bed Elemental Balance, wt.

Input	н	С	N	s	0	Ash	Total
Coal Moisture in coal Water of hydration Oxygen feed	4.24 0.84 0.1	63.48	1.11	3.51	7.68 6.76 0.82 7.2	11.46	91.48 7.6 0.92 7.2
Total	5.18	63.48	1.11	3.51	22.46	11.46	107.2
Output							
Pretreated coal, po Moisture in po Condensate Product gas Tar	2.95 0.16 1.1 0.22 0.41	54.98 2.64 3.92	1.07	2.95 0.85 0.24	7.54 1.26 8.8 5.23 0.33	12.45	81.94 1.42 9.9 8.94 4.9
Total	4.84	61.54	1.07	4.04	23.16	12.45	107.1
Recovery, %	93.4	96.9	96.4	115.1	103.1	108.6	99.9

Table 5. - Exit Gas Compositions on a Volume Percentage Basis

	40-atm. entrained	40-atm. fluidized-bed	70-atm. fluidized-bed
co ₂	1.16	3.18	1.7
СО	0.62	0.6	0.3
CH ₄		0.4	0.3
C2H4			trace
с ₂ н ₆		trace	0.1
с ₃ н ₆			trace
C3H8			trace
H ₂		0.2	trace
02	0.18	0.1	
H ₂ S		0.2	0.3
N ₂	Balance	Balance	Balance

Trace defined as <0.1 volume %.

Table 6. - Entrained Reactor Design-Basis Elemental Balance, wt.

Input	H	С	N	S	0	Ash	Total
Coal Moisture in coal Water of hydration Oxygen feed	4.5 0.69 0.1	64.25	1.22	3.47	8.4 5.51 0.79 11.18	11.07	92.91 6.2 0.89 11.18
Total	5.29	64.25	1.22	3.47	25.88	11.07	111.18
Output							
Pretreated coal, pc Moisture in pc Condensate Product gas	3.95 0.43 0.91	1.24	1.22	3.47	12.17 3.42 7.24 3.05	11.07	94.89 3.85 8.15 4.29
Total	5.29	64.25	1.22	3.47	25.88	11.07	111.18

Table 7. - 40-Atmosphere Fluidized-Bed Design-Basis Elemental Balance, wt.

Input	н	С	N	s	0	Ash	Total
Coal Moisture in coal Water of hydration Oxygen feed	4.5 0.69 0.1	64.25	1.22	3.47	8.4 5.51 0.79 8.64	11.07	92.91 6.2 0.89 8.64
Total	5.29	64.25	1.22	3.47	23.34	11.07	108.64
Output							
Pretreated coal, pc Moisture in pc Condensate Product gas Tar	3.89 0.08 1.12 0.09 0.11	1.96 1.04	1.22	3.17 0.24 0.06	9.26 0.64 8.92 4.43 0.09	11.07	89.86 0.72 10.04 6.72 1.3
Total	5.29	64.25	1.22	3.47	23.34	11.07	108.64

Table 8. - 70-Atmosphere Fluidized-Bed Design-Basis Elemental Balance, wt.

Input							
	н	С	N	s	0	Ash	Total
Coal Moisture in coal Water of hydration Oxygen feed	4.5 0.69 0.10	64.25	1,22	3.47	8.4 5.51 0.79 7.20	11.07	92.91 6.2 0.92 7.2
Total	5.29	64.25	1.22	3.47	21.9	11.07	107.2
Output							
Pretreated coal, pc Moisture in pc Condensate Product gas Tar	3.4 0.16 1.1 0.22 0.41	57.69 2.64 3.92	1.22	2.38 0.85 0.24	6.28 1.26 8.8 5.23 0.33	11.07	82.04 1.42 9.9 8.94 4.9
Total	5.29	64.25	1.22	3.47 •	21.9	11.07	107.2

Table 9. - Formation Reactions Used in Determining Heat of Reaction

Table 10. ~ Predicted Exit Stream Temperature Determined Through Energy Balances

	Predicted exit temperature	Observed exit
40-atm. entrained	401° C	353° C
40-atm. fluidized	419° C	401° C
70-atm. fluidized	427° C	419° C

Table 11. - Free Swelling Index Before and After Pretreatment

	Raw Coal	Pretreated Coal
40-atm. entrained	4.0	0.5
40-atm. fluidized	4.0	1.0
70-atm. fluidized	4.0	0

Table 12. - Comparison of Proximate Analyses of Pretreated Coals

	Feed coal	Entrained	Fluidized 40-atm.	Fluidized 70-atm.
Moisture	6.2	2.4	0.8	1.7
Volatile matter	39.3	33.7	35.9	26.2
Fixed carbon	43.5	49.0	50.4	57.2
Ash	11.0	14.9	13.6	14.9

Table 13 - Change in Sulfur Distribution During Entrained Pretreatment*

	Raw	Treated
Sulfate	0.43	0.35
Pyritic	1.05	1.3
Organic	2.37	2.32

^{*}values are percentage of coal sample on a moisture-free basis

References

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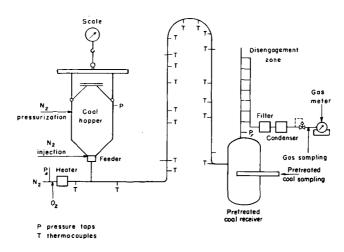


Figure-1 Schematic sketch of entrained pretreater PDU

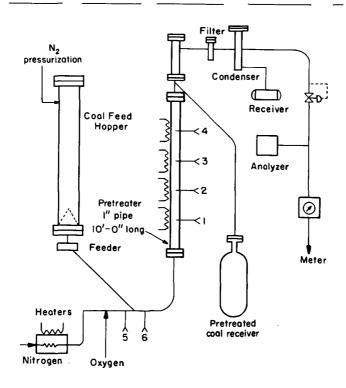
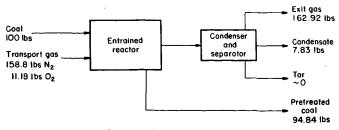


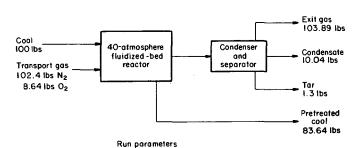
Figure 2-Schematic sketch of fluidized-bed coal pretreater PDU.



Run parameters

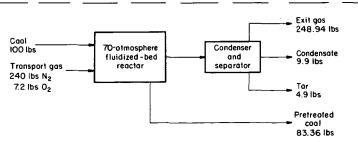
Coal rate =19.6 lbs/hr Superficial gas velocity =12.4 ft/sec Average operating temperature = 377 °C Maximum operating temperature = 485 °C

Figure 3 - Entrained reactor overall mass balance based on actual operating data.



Cool rate = 23.2 lbs /hr Superficial gas velacity = 1.08 ft/sec Average operating temperature = 401°C

Figure 4 - 40-otmosphere fluidized-bed reactor overall mass balance bosed on octual operating conditions.

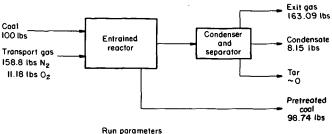


Run porometers

Coal rate =10.5 lbs/hr Superficial gas velocity = 0.68 ft/sec Average operating temperature = 419°C

Figure 5 - 70-atmosphere fluidized-bed reactor overall moss balance based on actual operating conditions.

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Run parameters

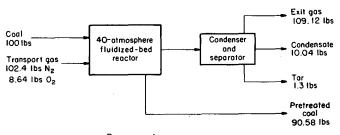
Cool rate =19.6 lbs/hr

Superficial gos velocity = 12.4 ft/sec

Average operating temperature = 377°C

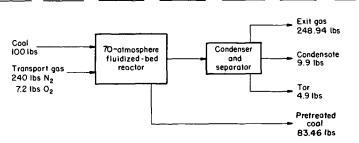
Maximum operating temperature = 485°C

Figure 6 - Typical, design - basis, entrained reactor mass balance.



Run porameters
Coal rate = 23.2 lbs/hr
Superficial gas velacity = 1.08 ft/sec
Average operating temperature = 401°C

Figure 7 - Typical, design - basis, 40-atmosphere fluidized - bed reactor mass balance.



Run parameters

Coal rate = 10.5 lbs /hr

Superficial gas velocity = 0.68 ft/sec

Average operating temperature = 419°C

Figure 8 - Typical , design - basis , 70-atmosphere fluidized - bed reactor mass balance.